

Statistical Thermodynamics in Chemistry and Biology

13. Chemical equilibria

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Chemical equilibria

This chapter:

- ▶ The goal of this chapter is to relate chemical equilibria to atomic structure through the molecular partition function.
 - ▶ Pressure and temperature dependence
 - ▶ Perturbation of equilibrium (Le Chatelier's principle)
 - ▶ The equilibrium between two states A and B ,



- ▶ The **equilibrium constant**, K is the ratio of the numbers (or concentrations) of particles in each of the two states at equilibrium.
- ▶ Two-state equilibria include: chemical isomerization, folding of biopolymers, binding of ligands to surfaces or macromolecules, condensation of vapour or freezing of a liquid

Condition for chemical equilibrium

- ▶ The equilibrium between two states A and B ,



- ▶ The direction of the arrow is important. We discuss in terms of **initial** and **final** state. The **equilibrium constant** is defined as

$$K = \frac{N_B}{N_A}$$

- ▶ Also written in terms of the **mol fraction**, x , and **probability**, p ,

$$K = \frac{x_B}{x_A} = \frac{p_B}{p_A} \quad \text{where} \quad x_A = p_A = \frac{N_A}{N_A + N_B}$$

- ▶ The Gibbs free energy is the preferred extremum principle,

$$dG = -SdT + Vdp + \mu_A dN_A + \mu_B dN_B$$

- ▶ At constant pressure ($dp = 0$) and temperature ($dT = 0$),

$$dG = \mu_A dN_A + \mu_B dN_B = 0$$

The condition for chemical equilibrium

Part 2

- ▶ The total number of particles, N , is preserved,

$$N_A + N_B = N \quad \Rightarrow \quad dN_A + dN_B = 0$$

- ▶ Condition for equilibrium rewritten as,

$$(\mu_A - \mu_B) dN_A = 0 \quad \Rightarrow \quad \mu_A = \mu_B$$

- ▶ So, the chemical potential, μ , has the same role for chemical equilibria as the temperature, T , for thermal equilibria, i.e. it is **equalized**.
- ▶ Our goal is to relate the chemical potential to the partition function.

Partition functions for chemical equilibria

- ▶ To simplify the notation later, denote the partition function q' ,

$$q' = \sum_{j=0}^t e^{-\beta \varepsilon_j} = e^{-\beta \varepsilon_0} + e^{-\beta \varepsilon_1} + \dots + e^{-\beta \varepsilon_t}$$

- ▶ Redefine the partition function as,

$$q = e^{\beta \varepsilon_0} q' = 1 + e^{-\beta(\varepsilon_1 - \varepsilon_0)} + e^{-\beta(\varepsilon_2 - \varepsilon_0)} + \dots + e^{-\beta(\varepsilon_t - \varepsilon_0)}$$

i.e. for q the ground state energy has been shifted from ε_0 to 0.

- ▶ The chemical potential in terms of the partition function, q' was given in Eq. 11.47,

$$\mu_A = -k_B T \ln \frac{q'_A}{N_A}$$

Note that Eq. 11.47 was derived for the canonical ensemble, but the result for $\frac{\partial G}{\partial N}$ will be the same.

Partition functions for chemical equilibria

Part 2

- ▶ Thus setting μ_A and μ_B equal,

$$\mu_A = -k_B T \ln \frac{q'_A}{N_A} = -k_B T \ln \frac{q'_B}{N_B} = \mu_B$$

gives the **equilibrium constant, K** as

$$K = \frac{N_B}{N_A} = \frac{q'_B}{q'_A} = \frac{q_B}{q_A} e^{-\beta(\varepsilon_0^B - \varepsilon_0^A)}$$

More complex equilibria

- ▶ General reaction,



where a , b , and c are the stoichiometrics of molecules A , B , C .
(E.g. $2H_2 + O_2 \rightarrow 2H_2O$).

- ▶ At constant p and T , the condition for equilibrium is,

$$dG = \mu_A dN_A + \mu_B dN_B + \mu_C dN_C = 0$$

- ▶ Stoichiometric constraints (mass conservation) are phrased in terms of a reaction coordinate, ξ ,

$$dN_C = c d\xi; \quad dN_B = -b d\xi; \quad dN_A = -a d\xi$$

- ▶ The equilibrium condition is rewritten as,

$$(c\mu_C - a\mu_A - b\mu_B) d\xi = 0$$

More complex equilibria

Part 2

- Expressing the chemical potential μ in terms of the partition function, q' ,

$$c \left(-k_B T \ln \frac{q'_C}{N_C} \right) = a \left(-k_B T \ln \frac{q'_A}{N_A} \right) + b \left(-k_B T \ln \frac{q'_B}{N_B} \right)$$

which leads to,

$$\left(\frac{q'_C}{N_C} \right)^c = \left(\frac{q'_A}{N_A} \right)^a \left(\frac{q'_B}{N_B} \right)^b$$

- Define the equilibrium constant, K , as

$$K = \frac{N_C^c}{N_A^a N_B^b} = \frac{(q'_C)^c}{(q'_A)^a (q'_B)^b} = \frac{q_C^c}{q_A^a q_B^b} e^{-\beta(c\varepsilon_0^C - a\varepsilon_0^A - b\varepsilon_0^B)}$$

- Define the **dissociation energy**, $D = -\varepsilon_0$, so that

$$-\Delta D = \Delta\varepsilon_0 = c\varepsilon_0^C - a\varepsilon_0^A - b\varepsilon_0^B$$

and

$$K = \frac{q_C^c}{q_A^a q_B^b} e^{\beta \Delta D}$$

Pressure-based equilibrium constants

- ▶ For ideal gases, it is more convenient to express the equilibrium constant in terms of the pressure.
- ▶ Employing the ideal gas law,

$$K = \frac{N_C^c}{N_A^a N_B^b} = \frac{\left(\frac{p_C V}{k_B T}\right)^c}{\left(\frac{p_A V}{k_B T}\right)^a \left(\frac{p_B V}{k_B T}\right)^b} = \frac{q_C^c}{q_A^a q_B^b} e^{\beta \Delta D}$$

- ▶ Multiply with $\left(\frac{V}{k_B T}\right)^{a+b-c}$, to get a new equilibrium constant, K_p ,

$$K_p = \frac{p_C^c}{p_A^a p_B^b} = (k_B T)^{c-a-b} \frac{q_{0C}^c}{q_{0A}^a q_{0B}^b} e^{\beta \Delta D}$$

where

$$q_0 = \frac{q}{V} = \frac{q_t}{V} q_r q_v q_e$$

Le Chatelier's principle

- ▶ Describes the response to a perturbation, i.e. a fluctuation of species B by dN_B .
- ▶ Return to the two-state equilibrium,



- ▶ The resulting change in the free energy, dG ,

$$dG = (\mu_B - \mu_A) d\xi$$

- ▶ $dG \leq 0$ implies that the system is driven back to equilibrium.
- ▶ One of the two terms, $(\mu_B - \mu_A)$ or $d\xi$, has to be negative.
- ▶ If a system is perturbed, it is driven back towards equilibrium.

Temperature dependence of equilibrium constants

van't Hoff equation

- ▶ Measure the equilibrium constant at different temperatures, $K(T)$.
- ▶ Example: two state equilibrium, $A \xrightarrow{K} B$
- ▶ At constant T and p , the condition for equilibrium is $\mu_A = \mu_B$.
- ▶ Thus for an ideal gas and recalling Eq. 11.50,

$$\mu_A^o + k_B T \ln p_A = \mu_B^o + k_B T \ln p_B$$

which gives

$$\ln K_p = \ln \frac{p_B}{p_A} = \frac{-(\mu_B^o - \mu_A^o)}{k_B T} = -\frac{\Delta\mu^o}{k_B T}$$

- ▶ Adopt partial molar properties, Eq. 9.32, ($\mu_j = h_j - Ts_j$),

$$\Delta\mu^o = \Delta h^o - T\Delta s^o$$

Temperature dependence of equilibrium constants

van't Hoff equation, part 2

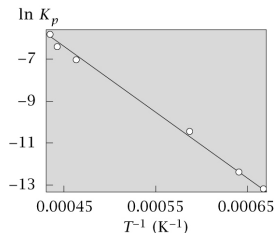
- ▶ The temperature dependence of K_p ,

$$\begin{aligned}\frac{\partial \ln K_p}{\partial T} &= -\frac{\partial}{\partial T} \left(\frac{\Delta \mu^o}{k_B T} \right) \\ &= -\frac{\partial}{\partial T} \left(\frac{\Delta h^o - T \Delta s^o}{k_B T} \right)\end{aligned}$$

- ▶ Approximating Δh^o and Δs^o as independent of temperature,

$$\frac{\partial \ln K_p}{\partial T} = \frac{\Delta h^o}{k_B T^2} \Rightarrow \frac{\partial \ln K_p}{\partial \frac{1}{T}} = -\frac{\Delta h^o}{k_B}$$

which is the **van't Hoff equation**. See figure for the dissociation of water.



Temperature dependence of equilibrium constants

Gibbs-Helmholtz equation

- ▶ Generalize the van't Hoff equation to any dependence $G(T)$. Rearrange $G = H - TS$ as,

$$H = G + TS = G - T \left(\frac{\partial G}{\partial T} \right)_p$$

- ▶ Use the following mathematical rearrangement,

$$\left(\frac{\partial \frac{G}{T}}{\partial T} \right)_p = \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_p - \frac{G}{T^2} = -\frac{1}{T^2} \left(G - T \left(\frac{\partial G}{\partial T} \right)_p \right)$$

- ▶ This leads to **Gibbs-Helmholtz equation**,

$$\left(\frac{\partial \frac{G}{T}}{\partial T} \right)_p = -\frac{H(T)}{T^2}$$

i.e. the temperature dependence of a Gibbs free energy can be obtained by measuring the enthalpy as a function of the temperature.

Temperature dependence of equilibrium constants

Gibbs-Helmholtz equation, part 2

- Similarly, for Helmholtz free energy,

$$\left(\frac{\partial \frac{F}{T}}{\partial T}\right)_V = -\frac{U(T)}{T^2}$$

Pressure dependence of the equilibrium constant

- ▶ Follow the procedure for the temperature dependence,

$$\frac{\partial \ln K(p)}{\partial p} = \frac{\partial}{\partial p} \left[-\frac{\mu_B^o - \mu_A^o}{k_B T} \right] = -\frac{1}{k_B T} \frac{\partial \Delta \mu^o}{\partial p}$$

- ▶ Use either Gibbs-Duhem equation, or, as here, a Maxwell relation,

$$\left(\frac{\partial \mu}{\partial p} \right)_{T,N} = \left(\frac{\partial V}{\partial N} \right)_{T,P} = v$$

where v is the partial molar volume.

- ▶ Thus,

$$\frac{\partial \ln K(p)}{\partial p} = -\frac{1}{k_B T} \frac{\partial (\mu_B^o - \mu_A^o)}{\partial p} = -\frac{v_B - v_A}{k_B T} = -\frac{\Delta v}{k_B T}$$

Pressure dependence of the equilibrium constant

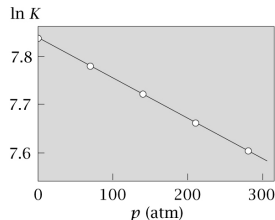
Example 13.6. Two state equilibrium

- ▶ Example: The partitioning of an anesthetic drug, *halothane*, between water (state *A*) and lipid bilayer membrane (state *B*), see the figure.
- ▶ Using the values of $(p, \ln K)$ of $(0, 7.84)$ and $(280, 7.6)$,

$$\Delta v = v_B - v_A = -RT \frac{\ln K_2 - \ln K_1}{p_2 - p_1}$$

$$= 21 \text{ cm}^3 \text{ mol}^{-1}$$

- ▶ Since $v_B - v_A > 0$, increasing the pressure shifts the equilibrium from *B* towards *A*.



Summary

- ▶ Equilibrium constants from atomic structure through the partition function.
- ▶ The temperature and pressure dependence of equilibrium constants.
- ▶ In Chapter 19, we will extend this to **chemical kinetics**, i.e. **rates of reactions**.

Exam June 2012 - Exercise 1

Solved a-c in chapter 10

Boltzmann distribution law

a) How is an *ensemble* defined in statistical thermodynamics? Discuss briefly the differences between the *microcanonical*, *canonical* and *isobaric-isothermal* ensembles. Which are the variables, fundamental function and extremum principle for each ensemble, respectively? Which ensembles are preferred experimentally (motivate the answer)?

b) For which ensemble is the Boltzmann distribution,

$$p_j = \frac{g_j e^{-E_j/k_B T}}{Q} \quad (1)$$

derived? What is g_j (we have also used the notation W_j) in eq. (1)? How is Q defined? What does the magnitude of Q tell us?

c) Assume that we have three molecules, $N = 3$, and also assume that only the two lowest molecular states, $\varepsilon_0 = \varepsilon$ and $\varepsilon_1 = 2\varepsilon$, can be occupied. What is the probability for that the total energy, E , is 5ε ? The temperature, $T = 300$ K and $\varepsilon = 10$ kJ/mol.

Exam June 2012 - Exercise 1

Part 2 - to be solved now

Boltzmann distribution law

d) The equilibrium constant, K ,

$$K = \frac{x_1}{x_2}$$

is investigated. Show that it can be written both in terms of the energy difference, $\Delta E = E_1 - E_2$, as

$$K = Ae^{-\Delta E/k_B T}$$

and in terms of the Helmholtz free energy difference, $\Delta F = F_1 - F_2$, as

$$K = e^{-\Delta F/k_B T}$$

Use eq. (1) as a starting point. Define A in terms of properties used in eq. (1).